AC IMPEDANCE AND VIBRATIONAL STUDIES OF BIOPOLYMER ELECTROLYTE CORNSTARCH:NH_4SCN

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ABSTRACT

Solid polymer electrolytes (SPEs) based on biopolymer play a vital role in creating materials for energy storage devices such as batteries and fuel cells. An attempt has been made to prepare solid polymer electrolyte using the biopolymer starch and the doping salt ammonium thiocyanate (NH4SCN) by solution casting technique with DMSO as solvent. The FTIR analysis confirms the complex formation between the polymer and salt. The AC impedance spectroscopy reveals that the biopolymer electrolyte 75 mol% of cornstarch: 25 mol % of NH4SCN has the maximum ionic conductivity 2.76x10-5 Scm-1 with low activation energy (0.32eV) among the prepared samples The ionic conductivity of the best conducting electrolyte increases with increase in temperature suggesting that the ionic conductivity is temperature dependent. The transport number measurement studies confirm that the ionic conductivity in these polymers is due to proton ions.

KEYWORDS: FTIR, AC impedance, Transport number.

A. Introduction:

Researches have utilized different starches like arrowroot, corn and potato starches. Corn starch is most popular polymer since it is renewable and bio degradable polymer. The polymer electrolyte based on potato starch doped with ammonium Iodide has the highest ambient temperature conductivity as 2.40×10^{-4} Scm^{-1}. [**Kumar et.al., 2012**].The aim of this work is to develop a proton conducting biopolymer electrolyte based on corn starch doped with ammonium thiocyanate. The prepared electrolytes have been characterized by FTIR analysis and electrochemical impedance spectroscopy in order to analyse the interactions between the polymer host (corn starch) and the charge carriers as well as the influence of the charge carriers on the ionic conductivity and conduction mechanism.

B. Preparation of Samples:

Cornstarch (AR grade, Sd fine chem) and NH_4SCN purchased from Spectrum have been used as starting materials to prepare proton conducting biopolymer electrolytes. Cornstarch: NH_4SCN based biopolymer electrolytes of various molar ratios such as (100: 0), (85: 15), (75: 25), and (65: 35) have been prepared by the solution casting technique. Appropriate quantity of Cornstarch and NH_4SCN are dissolved in the solvent dimethyl sulphoxide (DMSO) separately. Then these solutions are mixed together and stirred well to get homogeneous mixture. The resulting solution is poured on to glass petridishes and is allowed to vacuum dried in the vacuum oven for 5 days at 70^0C, in order to remove the solvent. The smooth uniform flexible polymer films which are transparent to visible light have been obtained.

FTIR studies

FTIR spectra have been recorded in the range of 4000 – 400 cm^{-1} using SHIMADZU IR Affinity -1 spectrophotometer to identify the complexation behavior of the prepared polymer electrolytes.

Conductivity measurements

AC conductivity measurements have been carried out on Cornstarch - NH_4SCN systems of uniform thickness having an area of 1 cm^2. Polymer electrolytes have been sandwiched between two stainless steel (SS) electrodes applying a potential of 1V from 42 Hz to 1 MHz using HIOKI make LCZ meter (model 3532) interfaced to a computer. The conductivity has been calculated from complex impedance plots of measured impedance (Z) and phase angle (θ). The temperature of the cell has been controlled using a thermostat and electrical measurements of the polymer electrolytes have been carried out in the temperature range 303K – 343K.

C. RESULTS AND DISCUSSIONS]

C.1 FTIR studies:

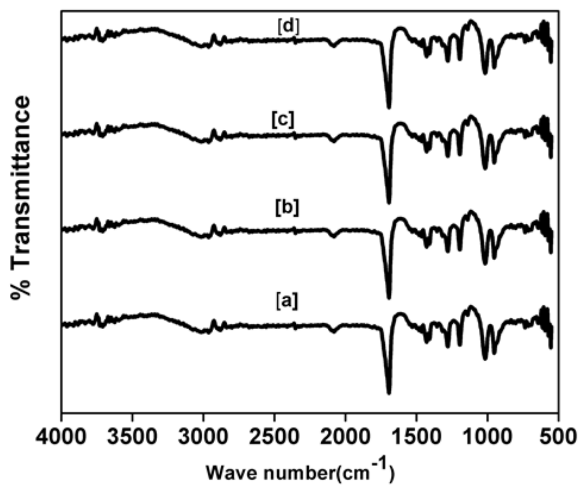

Figure 1: FTIR patterns of polymer electrolytes [a] Pure cornstarch [b] 85Cornstarch:15NH_4SCN [c] 75Cornstarch:25NH_4SCN [d] 65Cornstach:35NH_4SCN

The FTIR spectra of pure cornstarch and different molar ratios of NH_4SCN doped cornstarch complexes are shown in **Figure 1.** The hydroxyl band in the starch film appears at 1699 cm^{-1}. The

increasing NH_4SCN content has shifted the peak to lower wave numbers as shown in table 1. It indicates the strong interaction between NH_4SCN and cornstarch. The peak appears at 1027cm^{-1} is attributed to C-O bond stretching of the C-O-C group in the cornstarch. In Fig 1(b), with the addition of 15 mol% NH_4SCN, the peak shifted to 1014cm^{-1}. Further shifting has been observed with increasing salt content. On addition of 35 mol% NH_4SCN, the peak is located at 1021cm^{-1}. It may be due to interaction of NH_4^+ cation with oxygen atoms in the C-O-C group. The peaks at 2962cm^{-1} and 1280cm^{-1}are assigned to N-H symmetric stretching of NH_4^+ present in the salt NH_4SCN [**Yusof et.al.,2014**]. It gets shifted to lower wave number in the salt NH_4SCN added samples. All these results concluded that starch has interacted with NH_4SCN salt in this work.

Table 1.Vibrational peaks and assignments of (a) pure cornstarch (b) 85 cornstarch: 15NH_4SCN (c) 75cornstarch:25NH_4SCN (d) 65cornstarch:35NH_4SCN

Vibrational peaks of					Assignments
NH_4SCN (cm^{-1})	(100-X) Cornstarch: XNH_4SCN polymerelectrolytes (cm^{-1})				
	X = 0 mol %	X= 15 mol %	X = 25 mol %	X = 35 mol %	
3026	---	3020	3319	3313	N-H(asy) of NH_4^+
2962	---	2954	2927	2921	N-H(s) of NH_4^+
---	1699	1687	1693	1687	O-H stretching
1539	---	1533	1529	1535	N-H deformations(b)
---	1461	1483	1434	1434	O-H (b)
1280		1279	1279	1276	N-H(s) of NH_4^+
---	1027	1014	1015	1021	C-O(s)
---	823	810	823	822	C-H(r)

C.2 Conductance Spectra Analysis:]

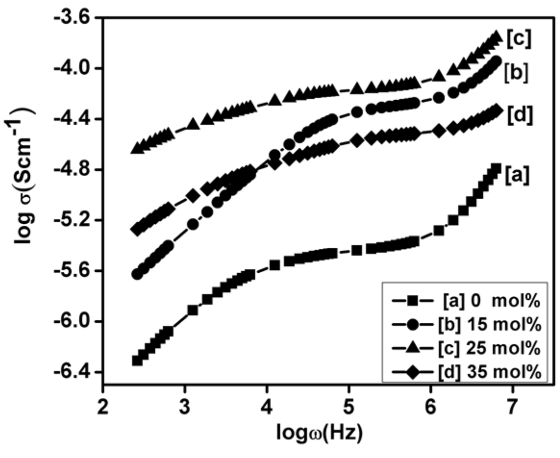

Figure 2: Conductance Spectra of [a] pure cornstarch[b] 85 cornstarch: 15NH_4SCN[c] 75cornstarch:25NH_4SCN [d] 65cornstarch: 35 NH_4SCN at 303K

The logarithmic plot of the conductivity as a function of angular frequency of (100 – X)Cornstarch: XNH_4SCN electrolytes at room temperature are shown in **Figure 2.** The low frequency dispersion region of the conductance spectra is associated with the space charge polarization at the blocking electrodes. The frequency independent plateau region is connected with the σ_{dc} of the polymer electrolyte. The extrapolation of the frequency independent plateau region to the log σ axis gives the dc conductivity of the electrolytes. The high Frequency region of the curve corresponds to the bulk relaxation phenomenon. The calculated dc conductivity of the electrolytes has been shown in the table 2.

Table-2 Ionic Conductivity, activation energy and transference numbers of (100-X)Cornstarch: XNH4SCN (X=0,15,25,35) electrolytes

Composition (Cornstarch:NH_4SCN) mol%	σ (10^{-5}Scm^{-1})	Activation energy (eV)	t_{ion}	t_{ele}
100:0	0.376	0.42	---	---
85:15	1.03	0.40	0.956	0.044
75:25	2.76	0.32	0.975	0.025
65:35	2.00	0.48	0.969	0.031

Figure 3 presents Conductance spectra of the best conducting electrolyte 75 cornstarch: 25 NH_4SCN at different temperatures. The maximum conductivity has been found to be 2.76×10^{-5} S cm^{-1} at 303K for 75cornstarch: 25NH_4SCN polymer electrolyte. It has been observed that the ionic conductivity increases with increases in temperature indicating that the ionic conductivity is temperature dependent.

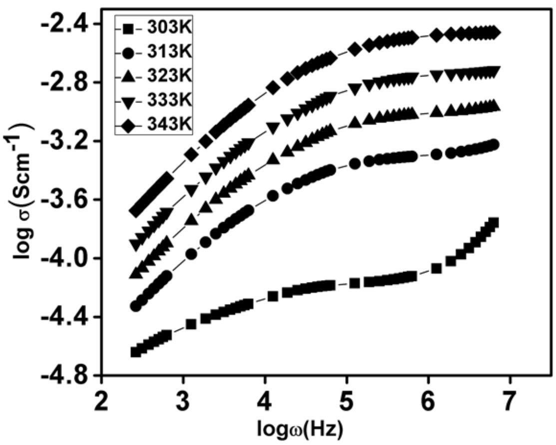

Figure 3: Conductance spectra of the best conducting electrolyte 75 cornstarch: 25 NH_4SCN at different temperatures.

C.3 Concentration Dependence Analysis

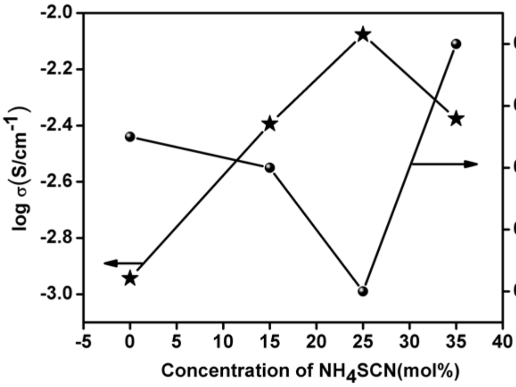

Figure 4: Variation of conductivity and activation energy as a function of NH_4SCN concentration.

The room temperature ionic conductivity and the activation energy of Cornstarch: NH_4SCN electrolytes as a function of salt concentration is presented in Figure 4.The highest ionic conductivity sample 75 Cornstarch: $25NH_4SCN$ has the lowest activation energy (0.32eV). The Lowest activation energy resulted from the short distance between transit sites provided by the biopolymer cornstarch leads to high ionic conductivity. It indicates that the ions in the highly conducting samples require lower energy for migration.

C.4 Dielectric Spectra Analysis

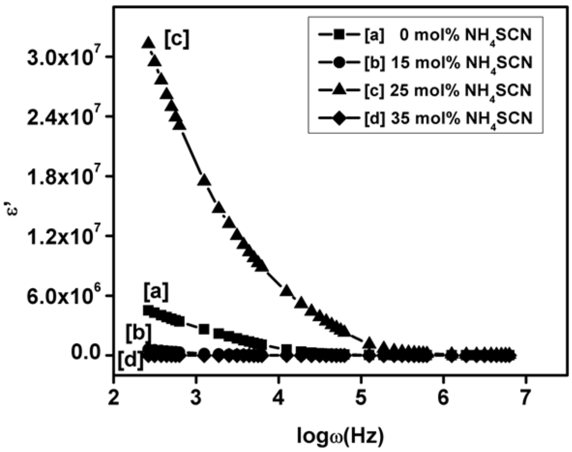

Figure 5 Dielectric constant vs. Frequency of [a] pure corn starch [b] 85corn starch: $15NH_4SCN$, [c] 75corn starch: $25NH_4SCN$, [d] 65corn starch: $35NH_4SCN$ polymer electrolytes at 303K respectively.

Figure 5 shows the frequency dependence of the dielectric constant ε' (ω) of [a] Pure corn starch [b] 85corn starch: $15NH_4SCN$, [c] 75corn starch: $25NH_4SCN$, [d] 65corn starch: $35NH_4SCN$ polymer electrolytes at 303K respectively. The values of dielectric constant are very high at low frequencies and relatively constant at higher frequencies. Such high value of ε may be due to the interfacial effects within the bulk of the biopolymer electrolyte [Vijaya et.al., 2013]. At higher frequencies, the periodic reversal of the electric field is in such a way that there is no excess ion diffusion in the field direction resulting in the decrease in dielectric constant.

C.5 Transport Number Measurements

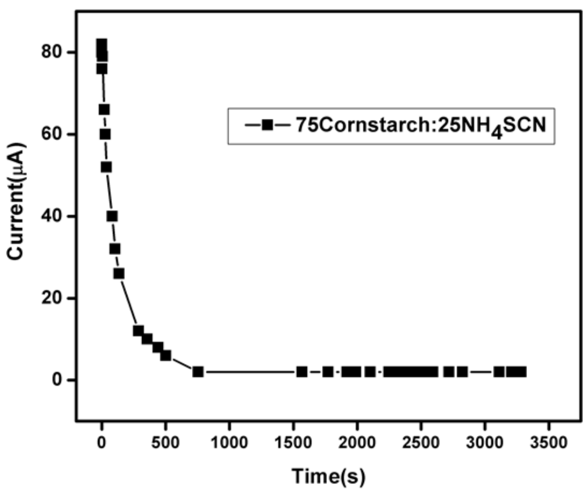

Figure 6 Polarization current as a function of time for 75Cornstarch:$25NH_4SCN$ polymer electrolyte.

The ionic transport number (t_{ion}) has been evaluated using Wagner's polarization technique [Wagner et.al., 1957]. In this technique, the DC current is monitored as a function of time on the application of a fixed DC voltage (1.5V) across the copper/Cornstarch: NHS_4CN biopolymer electrolyte/copper cell. The polarization current versus time plot of the best conducting electrolyte at room temperature is shown in **Figure 6.** The transference numbers (t_{ion}, t_{ele}) have been calculated using the equations

Ionic transference number (t_{ion}) = 1-I_f/I_i ....(6)

Electronic transference number (t_{ele}) = I_f/I_i ....(7)

where I_i and I_f are the initial and final current respectively. The calculated transference values are given in **Table 5.** For all compositions of polymer electrolytes, the values of ionic transference number t_{ion} are in the range 0.956 to 0.975. The current decreases with time reveal that the total conductivity of the polymer electrolytes is predominantly due to proton ions. Hence, it is proved that NH_4SCN salt has provided protons as mobile species in the polymer electrolyte systems.

D. CONCLUSION

The proton conducting biopolymer electrolytes consisting of cornstarch and ammonium thiocyanate of various compositions have been prepared by solutions casting technique.

- The FTIR analysis confirms the complex formation between the polymer Cornstarch and the salt NH_4SCN .
- The polymer electrolyte having 75mol%cornstarch with 25mol%$N_{H4}SCN$ has low activation energy and high ionic conductivity of $2.76x1^{0-5}$ S/cm at 303K.
- Conductance spectra analysis reveals that the ionic conductivity increases with increases in temperature indicating that the ionic conductivity is temperature dependent.
- From Wagner's polarization technique, total conductivity of the polymer electrolytes is predominantly due to proton ions with negligible contribution of electrons. It concludes that the prepared biopolymer electrolytes are proton conductors.

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